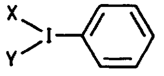
Formation of Aryliodine(III) Derivatives in the Nitration of Aryl Iodides in Acetic Anhydride

Gordon W. Bushnell, Alfred Fischer,* and Prabha N. Ibrahim
Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

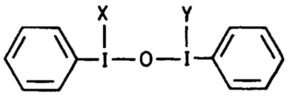
Nitration of iodobenzene, *o*-iodotoluene, and *p*-iodotoluene in acetic anhydride results in reversible oxidation to aryliodine(III) compounds prior to the formation of the expected nitro derivatives. μ-Oxo-[nitrato(phenyl)iodine][phenyl(trifluoroacetato)iodine] has been isolated from nitration of iodobenzene and its crystal structure determined.

When *o*- and *p*-iodo-toluene are nitrated in acetic anhydride the reactions do not go to completion under conditions which bring about complete reaction of the other halogenotoluenes and the iodotoluenes appear to be less reactive than the other halogenotoluenes. This is surprising since nitration of iodobenzene in aqueous sulphuric acid is faster than nitration of the other halogenobenzenes[1] and additivity of substituent effects would suggest that this should also be true of the iodotoluenes. Nitration of *p*-fluoro-, *p*-chloro-, and *p*-bromotoluene in acetic anhydride gives good yields of adducts with nitro *ipso* to methyl and lesser amounts of the nitro substitution products.[2,3] The calculated product distribution for the nitration of *p*-iodotoluene is similar to that for *p*-bromotoluene; however, little adduct is formed from *p*-iodotoluene.[2] Parallel observations have been made on the *ortho*-halogenotoluenes *viz.* 1,4-adducts are formed in significant yield from the fluoro, chloro, and bromo derivatives but not from the iodo compound.[4] We have investigated the nitration of *o*- and *p*-iodotoluene and of iodobenzene and have resolved these apparent anomalies.



(1)

a; X = Y = $OCOCF_3$
b; X = Y = ONO_2
c; X = ONO_2, Y = $OCOCF_3$
d; X = Y = OAc
e; X = OAc, Y = $OCOCF_3$
f; X = OAc, Y = ONO_2



(2)

a; X = Y = $OCOCF_3$
b; X = Y = ONO_2
c; X = ONO_2, Y = $OCOCF_3$

Results and Discussion

Nitration Reactions.—o-Iodotoluene. Nitration was carried out using a mixture of nitric acid, acetic anhydride, and trifluoroacetic anhydride and was followed by ^1H n.m.r. spectroscopy. At −20 °C the *o*-iodotoluene reacted completely over a period of 30 min. The major component of the product mixture had ^1H n.m.r. peaks similar to those of *o*-iodotoluene but shifted approximately δ 0.5 downfield. Some 2-iodo-4-nitro- and 2-iodo-5-nitro-toluene were also formed and a minor amount (<10% of the product) of diene adduct. When the reaction mixture was worked-up after this time the major component of the isolated product mixture was *o*-iodotoluene and the major component in the reaction mixture was not present. When the reaction was carried out for an extended period (15 h) at low temperature, or for a shorter period (20 min) at ambient temperature, the first formed product disappeared and the iodonitrotoluenes were obtained. It is evident that the *o*-iodotoluene was initially converted reversibly into an intermediate from which the *o*-iodotoluene was regenerated as it was nitrated, or when the mixture was worked up. By analogy with the reaction of iodobenzene (below) this intermediate is assumed to be an *o*-iodosyltoluene derivative similar to (**1**). When the nitration was carried out in the absence of trifluoroacetic anhydride the reactions were similar although much slower, even at 0 °C, and the iodotoluene disappeared over 15 h. Again an intermediate was formed and nitration ensued.

p-*Iodotoluene.* Nitration was carried out with nitric acid in acetic anhydride. As in the case of *o*-iodotoluene an intermediate was formed which regenerated the iodotoluene on work-up and which, in the reaction solution, was in equilibrium with the iodotoluene since nitration to a mixture of *p*-nitrotoluene, 4-iodo-2-nitro-, and 4-iodo-3-nitro-toluene slowly ensued. Some diene adduct (<20%) was also formed.

Iodobenzene. A mixture of nitric acid, acetic anhydride, and trifluoroacetic anhydride was used for nitration. At −20 °C the iodobenzene reacted completely over 40 min. Apart from the singlet of *p*-iodonitrobenzene the n.m.r. of the solid which crystallized out was identical with that of bis(trifluoroacetoxyiodo)benzene (**1a**). The n.m.r. of the reaction mixture was similar except that it appeared to reflect the presence of two iodosylbenzene derivatives with slightly different chemical shifts. Trituration of the crystals with ether at ambient temperature left a crystalline residue (2.5%) which was identified as μ-oxo[nitrato(phenyl)iodine][phenyl(trifluoroacetato)iodine] (**2c**). After 15 h at ambient temperature a sample of the reaction mixture had the following composition, *p*-iodonitrobenzene (13%) and the iodosylbenzene derivatives (87%). After 4 months at −20 °C the mixture was *p*-iodonitrobenzene (40%) and iodobenzene (60%). Work-up of the reaction mixture after 40 min gave iodobenzene (95%) and *p*-iodonitrobenzene (5%) and these products were also obtained when a portion of the substance which had crystallized from the reaction mixture was worked up. A 10% solution of this substance in ether reverted to the mixture (95:5) of iodobenzene and *p*-iodonitrobenzene over 3 days. A solution in dichloromethane was more stable but developed 35% of iodobenzene in the same time.

Nitration was also carried out with nitric acid in acetic anhydride. The n.m.r. spectra of the reaction mixture exhibited peaks for a single iodosylbenzene derivative and *p*-iodonitrobenzene was also present. When iodobenzene was nitrated with nitric acid in dichloromethane no intermediate was observed and *p*-iodonitrobenzene was formed.

The simplest explanation for the observation of one phenyliodine(III) derivative in the acetic anhydride solution and two in the mixed anhydride solution is that (diacetoxyiodo)benzene (**1d**) is formed in the former and both (**1a**) and (**1d**) in the

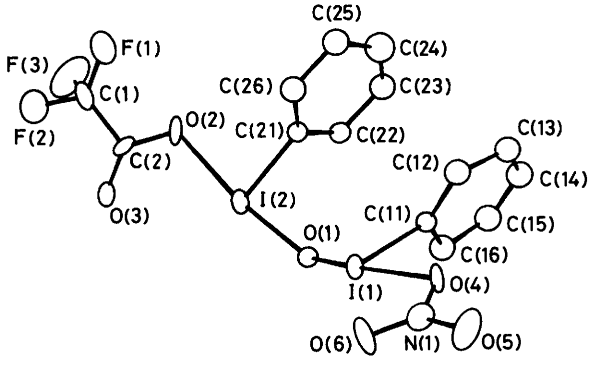


Figure. The molecular structure of μ-oxo[nitrato(phenyl)iodine]-[phenyl(trifluoroacetato)iodine] (**2c**)

Table 1. Fractional atomic co-ordinates (× 10^4)[a]

Atom	*x*	*y*	*z*
I(1)	6 240.1(8)	−438.4(13)	−278(2)
I(2)	6 075.5(8)	939.6(14)	−4 104(2)
F(1)	4 790(14)	4 174(20)	−6 540(29)
F(2)	4 154(11)	3 122(17)	−8 233(30)
F(3)	5 048(15)	3 730(24)	−8 710(33)
O(1)	6 526(8)	−250(12)	−2 473(18)
O(2)	5 692(8)	2 472(14)	−5 724(19)
O(3)	4 983(9)	1 273(18)	−7 333(21)
O(4)	6 199(9)	−671(16)	2 540(17)
O(5)	5 626(10)	−1 486(18)	4 185(24)
O(6)	5 252(10)	−1 566(17)	1 541(23)
N(1)	5 672(14)	−1 279(20)	2 719(31)
C(1)	4 777(16)	3 278(25)	−7 473(36)
C(2)	5 174(14)	2 229(23)	−6 845(29)
C(11)	7 193(11)	295(18)	824(28)
C(12)	7 183(14)	1 221(22)	2 024(33)
C(13)	7 859(15)	1 599(23)	2 788(35)
C(14)	8 439(16)	1 100(24)	2 348(37)
C(15)	8 441(16)	247(25)	1 145(38)
C(16)	7 761(14)	−252(22)	427(33)
C(21)	6 562(11)	2 250(18)	−2 566(27)
C(22)	7 294(12)	2 217(19)	−2 250(29)
C(23)	7 628(14)	3 052(22)	−1 049(32)
C(24)	7 267(17)	3 789(27)	−491(39)
C(25)	6 518(16)	3 901(25)	−823(37)
C(26)	6 157(14)	3 062(23)	−1 901(36)

[a] Estimated standard deviations are given in parentheses.

latter. This interpretation is supported by the similarity of the n.m.r. spectra of the reaction mixture and a solution of a mixture of authentic (**1a**) and (**1d**) and the fact that the solid which crystallized from the mixed anhydride solution was shown to be (**1a**). However, (dinitratoiodo)benzene (**1b**) is also a possible product in both reactions as is the mixed derivative (**1f**) and, in the trifluoroacetic anhydride solutions, (**1c**) and (**1e**). Some nitrato derivative must be present as an intermediate in the formation of (**2c**).

(Diacetoxyiodo)benzene (**1d**). Reaction of (**1d**) with a mixture of nitric acid, acetic anhydride, and trifluoroacetic anhydride in dichloromethane at −20 °C resulted in its partial conversion into (**1a**) (~60%) which crystallized out. At ambient temperature over 15 h the iodine(III) derivatives were partially converted into iodobenzene (~50%) and a small amount of *p*-iodonitrobenzene (5%).

The formation of iodosylbenzene derivatives has been extensively investigated.[5–11] The acetate exists preferentially in the monomeric or non-bridged form (**1d**), the trifluoroacetate exists in both non-bridged (**1a**) and dimeric or bridged forms (**2a**),[7] and both forms of the nitrate have been prepared although the non-bridged form (**1b**) is readily hydrolysed to the bridged form (**2b**) and the latter is the more readily obtained.[11] The bridged and non-bridged compounds are readily distinguished by n.m.r. spectroscopy. The peaks of (**2a**) are at higher field than the peaks of (**1a**) and the lower field peaks of (**2a**) occur in a region where (**1a**) has no absorption.[5] We found that (**2b**) and (**2c**) likewise absorb at higher field than do (**1b**)[11] and (**1d**). No detectable amount of bridged compound was formed in the anhydride nitration solutions. The small amount of (**2c**) that was isolated may have been present but undetected in the reaction solutions or may have been formed during the process of isolation. Alcock and Waddington[7] pointed out that (**2b**) can be considered as the half-hydrolysis product of (**1b**) and, as mentioned, the reaction has been observed.[11] If reaction of (**1**) with water is generally the mode of formation of (**2**) then it is not surprising that no (**2**) is obtained in anhydride solutions. We attempted to prepare (**1b**) by reaction of (**1d**) with nitric acid in dichloromethane. After removal of the solvent the viscous residue had the characteristic n.m.r. peaks for the non-bridged compound and contained approximately one acetate group per aromatic ring, corresponding to the formula for (**1f**). When this substance was dissolved in dichloromethane and allowed to crystallize slowly (**2b**) was formed. Crystals of (**2b**) were also slowly formed when the oil was allowed to stand at ambient temperature. However, when the sample was allowed to stand for a week *p*-iodonitrobenzene was obtained. Compound (**2b**) on reaction with (**1a**) and sodium methoxide gave (**2c**).

The nitrating ability of (**2c**) was investigated using activated substrates. No reaction occurred between (**2c**) and mesitylene. With phenols in dichloromethane (**2c**) was reduced to iodobenzene and the phenols (*o*-cresol, hydroquinone) oxidized to quinones.

Conclusions. Our results demonstrate that aryl iodides are rapidly and reversibly oxidized to aryliodine(III) derivatives by nitric acid in anhydride solutions. Presumably the nitric acid is reduced to nitrous acid. The reaction accounts for the slowness of nitration of aryl iodides in acetic anhydride; little aryl iodide is available to be nitrated. The opportunity for *ipso* nitration of the iodotoluenes is similarly reduced. Iodine(III) compounds do not appear to be formed when the aryl iodides are nitrated under other conditions and the iodides exhibit normal reactivity. The formation of the diacyl esters may provide a driving force for the oxidation reaction. A surprising feature of our results is the ease of reduction of the iodine(III) compounds on work-up (involving washing with aqueous solutions) or on standing in ether solution. This last reaction may also involve reaction with water absorbed from the atmosphere. It is possible that nitrite or nitrous acid is present in these situations and is the active reducing agent. Bridged iodine(III) compounds exemplified by (**2c**), whose crystal structure is described in the next section, do not appear to be primary reaction products but are formed *via* the non-bridged compounds. Compound (**2c**) is the first example of a non-symmetrical iodosylbenzene bridged compound.

Crystal Structure of (**2c**).—A drawing of the molecule with the atom-labelling scheme is given in the Figure. The thermal ellipsoids are surfaces of equal probability containing 25% of the total probability. Compounds (**2c**) contains both of the ligands present in (**2a**) and (**2b**). The crystal structures of (**2a**) and (**2b**) (α-form) are known.[5,6] The bond lengths (Table 2) and angles (Table 3) for (**2c**) are very similar to the corresponding values in (**2a**) and (**2b**). The interesting difference between the I–O bridge bonds and the I–O anion bonding has already been discussed.[5] Our results confirm that the I–O trifluoroacetate bond [2.264(14) Å] is shorter than the I–O nitrate bond [2.354(15) Å].

Each iodine centre has a T-shaped co-ordination geometry.

Table 2. Interatomic distances (Å)

Atoms	Distance	Atoms	Distance
O(1)–I(1)	1.999(16)	O(1)–I(2)	2.012(14)
C(11)–I(1)	2.10(2)	C(21)–I(2)	2.09(2)
O(4)–I(1)	2.354(15)	O(2)–I(2)	2.264(14)
C(12)–C(11)	1.46(3)	C(22)–C(21)	1.41(3)
C(13)–C(12)	1.43(4)	C(23)–C(22)	1.45(3)
C(14)–C(13)	1.38(4)	C(24)–C(23)	1.25(4)
C(15)–C(14)	1.40(4)	C(25)–C(24)	1.45(4)
C(16)–C(15)	1.47(4)	C(26)–C(25)	1.42(4)
C(16)–C(11)	1.37(3)	C(26)–C(21)	1.40(3)
C(2)–O(2)	1.27(3)	C(2)–C(1)	1.48(4)
C(2)–O(3)	1.21(3)	C(1)–F(1)	1.29(3)
N(1)–O(4)	1.28(3)	C(1)–F(2)	1.28(3)
N(1)–O(5)	1.25(3)	C(1)–F(3)	1.34(4)
N(1)–O(6)	1.20(2)		

[a] Estimated standard deviations are given in parentheses.

Table 3. Bond angles (°)[a]

Atoms	Angle	Atoms	Angle
C(11)–I(1)–O(4)	78.8(8)	C(1)–C(2)–O(2)	111.8(24)
O(1)–I(1)–O(4)	166.0(6)	C(1)–C(2)–O(3)	121.3(25)
O(1)–I(1)–C(11)	88.6(8)	C(12)–C(11)–I(1)	118.0(17)
C(21)–I(2)–O(2)	81.8(7)	C(16)–C(11)–I(1)	114.0(17)
O(1)–I(2)–O(2)	171.1(6)	C(16)–C(11)–C(12)	127.7(22)
O(1)–I(2)–C(21)	89.6(7)	C(13)–C(12)–C(11)	113.5(23)
I(2)–O(1)–I(1)	121.2(8)	C(14)–C(13)–C(12)	119.8(26)
C(2)–O(2)–I(2)	113.0(15)	C(15)–C(14)–C(13)	126.1(28)
N(1)–O(4)–I(1)	110.4(14)	C(16)–C(15)–C(14)	116.3(28)
O(5)–N(1)–O(4)	114.6(24)	C(15)–C(16)–C(11)	115.9(24)
O(6)–N(1)–O(4)	120.6(22)	C(22)–C(21)–I(2)	115.4(17)
O(6)–N(1)–O(5)	124.7(26)	C(26)–C(21)–I(2)	119.6(17)
F(2)–C(1)–F(1)	108.6(29)	C(26)–C(21)–C(22)	125.0(21)
F(3)–C(1)–F(1)	100.0(26)	C(23)–C(22)–C(21)	115.3(22)
F(3)–C(1)–F(2)	99.0(24)	C(24)–C(23)–C(22)	119.3(26)
C(2)–C(1)–F(1)	119.8(24)	C(25)–C(24)–C(23)	127.9(30)
C(2)–C(1)–F(2)	116.7(25)	C(26)–C(25)–C(24)	115.6(29)
C(2)–C(1)–F(3)	109.3(28)	C(25)–C(26)–C(21)	116.7(25)
O(3)–C(2)–O(2)	126.8(21)		

[a] Estimated standard deviations are given in parentheses.

The distribution of the two lone pairs on each iodine atom and the three bonding electron pairs is trigonal bipyramidal. The central feature of the molecule is the V-shape of the I–O–I bridge with an angle of 121.2(8)°. The larger V-shape O–I–O–I–O is a non-planar set of atoms. Table 4 gives the least-squares planes and torsion angles and shows that there is non-planarity in the T-shaped co-ordination. However, the least-squares planes of the iodine co-ordination are equally inclined at 110.0 and 109.8° to the I–O–I bridge plane. Electron pair repulsion theory would predict that since the lone pairs are more voluminous than the bonding pairs, the O–I–O groups would be distorted from linearity with O(2) and O(4) on the same side of the V-bridge as the phenyl groups. The deviations from the plane are $-0.35(2)$ and $-0.41(2)$° in the direction expected. The departure of the T-shaped iodine co-ordination from planarity might be explained by the difference between the lone-pair repulsions [I(1) to I(2)]. That above the V would be more severe than that below, so O(4) is found on the same side of plane 2 as C(16), and O(2) is found on the same side of plane 3 as C(22). We would expect the overall conformation to be decided by both lone pair and phenyl ring interactions between the two iodine centres. The distance I(1) to I(2) is 3.496 Å, and the distance between the phenyl ring centres is 3.927 Å. The angle between the I(1)–C(11) and the I(2)–C(21) bonds is 34.7°. The phenyl ring planes are at 53.5 and 61.3° to their own T-planes, but only 5.8° from each other, which is near to parallel.

Sufficient information is given in Table 4 to define the positions of the nitate and trifluoroacetate ligands which are understandable in terms of conventional bonding theory. The main co-ordinate bonds of the anions are close to expected lone-pair directions. It is noteworthy however that the least-squares plane of the C and O atoms of the trifluoroacetate passes 0.713 Å below I(2), whereas the plane of the nitrate lies 0.148 Å from I(1).

Finally, we observe both intra- and inter-molecular weak secondary bonding to the iodine atoms. Both anions are asymmetrically bidentate; O(3) weakly co-ordinates to I(1) of an inverted and shifted molecule; O(5) of the nitrate weakly interacts with I(2) of a molecule translated by one unit cell in the *z*-direction. These interactions occur on the opposite side of the iodine atoms to the phenyl rings. The interatomic distances for **(2c)** are similar to those found in **(2a)** and **(2b)**, but the crystal packing is different in the three compounds and this seems to have a significant effect in determining the conformations observed in the various crystals. There are no obvious similarities between the unit-cell dimensions of the three crystals. The crystal structure of **(2a)** shows a molecule with phenyl groups on opposite sides of the V-bridge. The crystal structure of **(2b)** has the phenyl groups on the same side of the V but, unlike **(2c)**, the phenyl groups are far from parallel.

Experimental

General experimental methods have been described previously.[2] (Diacetoxyiodo)benzene was from Aldrich. Bis(trifluoroacetoxyiodo)benzene[7] was prepared by stirring (diacetoxyiodo)benzene with trifuoroacetic acid for 15 min followed by evaporation of the excess of acid, m.p. (CH_2Cl_2) 120—122 °C (lit.,[12] 119—122 °C); $\nu_{max.}$ 1 730 and 1 700 cm^{-1} (CO); δ(250 MHz; $CDCl_3$) 7.62 (2 H, *J* 7.3 and 8.1 Hz, 3-and 5-H), 7.74 (1 H, *J* 7.3 Hz, 4-H), and 8.20 (2 H, *J* 8.1 Hz, 2-and 6-H).

Nitration Reactions.—o-Iodotoluene. Reactions were carried out using a mol ratio of substrate:nitric acid:acetic anhydride:trifluoroacetic anhydride = 1:2:5:2. The nitrating mixture was added to a solution of the *o*-iodotoluene (1.1 g, 5 mmol) in dichloromethane or acetic anhydride (1 cm^3) at -40 °C and the ensuing reaction was monitored by ^1H n.m.r. spectroscopy generally at -20 °C. *o*-Iodotoluene had ^1H n.m.r. peaks centred at δ 6.9, 7.2, and 7.8 whereas the initially formed product had peaks at δ 7.35, 7.6, and 8.35. The presence of 2-iodo-5-nitrotoluene (δ ~8.0) and of 2-iodo-4-nitrotoluene (δ 8.55) was evident. The diene adduct had peaks at δ 6.2—6.3 (observed in solutions to which no dichloromethane had been added, or in worked up solutions which also exhibited methyl peaks at δ 1.80 and 1.90 and acetate peaks at δ 2.08 and 2.10). Reactions were worked up by pouring into ether (10 cm^3) at -40 °C and then washing with cold ammonium hydroxide (5 cm^3; 28%) followed by water. The ether solution was dried ($MgSO_4$), the ether evaporated, and the residue analysed by ^1H n.m.r. spectroscopy. When a reaction was carried out on a 25 mmol scale at ambient temperature for 20 min substantially all of the *o*-iodotoluene was converted into nitration product containing *o*-nitro-:2-iodo-3-nitro-:2-iodo-4-nitro-:2-iodo-5-nitro-:2-iodo-6-nitro-toluene = 11:13:14:56:7 (5.4 g). After extraction with 5% ether–light petroleum (b.p. 30—60 °C) the residue (2.3 g) was recrystallized from ether–light petroleum (b.p. 30—60 °C) to give 2-iodo-5-nitrotoluene, m.p. 102 °C (lit.,[13] m.p. 103 °C); δ(250 MHz; $CDCl_3$) 2.54 (3 H, s, Me), 7.72 (1 H, dd, *J* 2.4 and 8.5 Hz, 4-H), 8.00 (1 H, d, *J* 8.5 Hz, 3-H), and 8.07 (1 H, d, *J* 2.4 Hz, 6-H). The extract on h.p.l.c. on silica with 5% ether–light petroleum (b.p. 30—60 °C) as eluant gave, in

Table 4. Least-squares planes and torsion angles *

(a) Definition of the planes

Plane	Atoms	Description	χ^2
1	I(1), O(1), I(2)	Main V	—
2	O(1), I(1), O(4), C(11)	1st T	103
3	O(1), I(2), O(2), C(21)	2nd T	16
4	C(11)–C(16)	Phenyl ring 1	7.4
5	C(21)–C(26)	Phenyl ring 2	3.9
6	N(1), O(4)–O(6)	Nitrate	0.60
7	O(2), O(3), C(1), C(2)	Perfluoroacetate	0.66

(b) Angles between the planes (°)

1, 2 = 110.0	1, 3 = 109.8	1, 4 = 103.5	1, 5 = 103.4	1, 6 = 75.6	1, 7 = 102.6
	2, 3 = 113.6	2, 4 = 53.5	2, 5 = 59.2	2, 6 = 170.5	2, 7 = 101.0
		3, 4 = 66.9	3, 5 = 61.3	3, 6 = 57.0	3, 7 = 19.5
			4, 5 = 5.8	4, 6 = 118.4	4, 7 = 49.8
				5, 6 = 112.6	5, 7 = 44.0
					6, 7 = 69.9

(c) Perpendicular distances of atoms from the least-squares planes (Å)

Plane
1 O(2), −0.35(2); O(4), −0.41(2); F(1), −0.38(2); C(11), −1.99(2); C(21), −1.96(2).
2 I(1), 0.002(2); O(4), −0.11(2); C(11), 0.05(2); O(1), −0.104(14); C(12), 1.08(3); C(14), −0.05(3); N(1), −0.33(2); O(5), −0.46(2); O(6), −0.33(2).
3 I(2), −0.001(2); O(2), 0.05(2); C(21), −0.01(2); O(1), 0.04(2); C(22), 1.10(2); C(24), 0.07(3); C(1), −0.72(3); C(2), −0.28(3); O(3), −0.30(2).
6 I(1), 0.148(2); O(1), 0.52(1); I(2), −0.915(2); C(11), 0.30(2); C(14), 0.64(3).
7 I(2), −0.713(2); I(1), 3.202(2); O(1), −1.31(2); C(22), −0.17(2); F(3), 1.25(3); F(1), −0.54(3); F(2), −0.37(2).

(d) Torsion angles (°)

O(5)–N(1)–O(4)–I(1)	177(2)	F(1)–C(1)–C(2)–O(2)	26(4)
O(6)–N(1)–O(4)–I(1)	6(3)	F(2)–C(1)–C(2)–O(2)	161(3)
C(1)–C(2)–O(2)–I(2)	159(2)	F(3)–C(1)–C(2)–O(2)	88(3)
O(3)–C(2)–O(2)–I(2)	17(4)	F(1)–C(1)–C(2)–O(3)	150(3)
N(1)–O(4)–I(1)–C(11)	173(2)	F(2)–C(1)–C(2)–O(3)	16(4)
C(2)–O(2)–I(2)–C(21)	163(2)	F(3)–C(1)–C(2)–O(3)	95(3)
C(11)–I(1) ··· I(2)–C(21)	34.7(9)		

* $\chi^2 = \Sigma[P_i^2/\sigma^2(P_i)]$ where the summation is over all atoms in the plane, and P_i is the perpendicular distance of atom *i* from the plane.

sequence, *o*-iodotoluene, a mixture of *o*-nitro-, 2-iodo-4-nitro-, 2-iodo-5-nitro-, and 2-iodo-6-nitro-toluene, 2-iodo-4-nitrotoluene, and 2-iodo-3-nitrotoluene. After recrystallization from ether–light petroleum (b.p. 30—60 °C) 2-iodo-4-nitrotoluene had m.p. 60 °C (lit.,[13] m.p. 61 °C); δ(250 MHz; $CDCl_3$) 2.54 (3 H, s, Me), 7.38 (1 H, d, *J* 8.4 Hz, 6-H), 8.11 (1 H, dd, *J* 2.3 and 8.4 Hz, 5-H), and 8.65 (1 H, d, *J* 2.3 Hz, 3-H); 2-iodo-3-nitrotoluene had m.p. 66 °C (lit.,[13] m.p. 67—68 °C); δ(250 MHz; $CDCl_3$) 2.58 (3 H, s, Me), 7.34—7.44 (3 H, m, 4-, 5-, and 6-H).

p-*Iodotoluene*. A mol ratio of substrate:nitric acid:acetic anhydride = 1:5:20 was used. The nitrating mixture was added to a solution of the *p*-iodotoluene (0.44 g, 2 mmol) in acetic anhydride (1 cm^3) at −40 °C and the reaction was followed at −20 °C. The initially formed intermediate exhibited an AB quartet with the doublets centred at δ 7.45 and 8.2. The development of this intermediate, the disappearance of *p*-iodotoluene (δ 7.0 and 7.6), and the formation of *p*-nitrotoluene (δ 7.25 and 8.1) were readily observed. As nitration became more extensive the formation of both 4-iodo-2-nitro- and 4-iodo-3-nitro-toluene could be seen. Diene adducts were observed (δ 6.4). The reaction mixture was worked-up as described for *o*-iodotoluene. In a reaction carried out at ambient temperature for 20 min complete nitration occurred to give *p*-nitro-:4-iodo-2-nitro-:4-iodo-3-nitro-toluene = 50:30:20.

Iodobenzene. Reactions were carried out using a mol ratio of substrate:nitric acid:acetic anhydride:trifluoroacetic anhydride = 1:3:5:2. The nitrating mixture was added to a solution of the iodobenzene (1.0 g, 5 mmol) in dichloromethane (1 cm^3) at −40 °C and the ensuing reaction was monitored by ^1H n.m.r. spectroscopy at −20 °C. The initially formed product had ^1H n.m.r. peaks centred at δ 7.64 (large peak of multiplet) and δ 8.26 (triplet). After 40 min the iodobenzene had reacted completely and crystallization had occurred. *p*-Iodonitrobenzene (δ 7.9, s) was also formed as a minor product. Work-up at this point as described above gave iodobenzene and *p*-iodonitrobenzene. Alternatively the crystalline material was isolated by cooling the mixture to −78 °C followed by filtration. The residue was washed with cold light petroleum (b.p. 30—60 °C). In a reaction carried out on a 37 mmol scale one quarter of the washed residue was triturated with ether (10 cm^3) at ambient temperature and the residue (103 mg) was recrystallized from dichloromethane to give (**2c**), m.p. 118 °C (decomp.) (Found: C, 28.0; H, 1.7; F, 9.6; N, 2.4. $C_{14}N_{10}F_3I_2NO_6$ requires C, 28.1; H, 1.7; F, 9.5; N, 2.3%); δ(90 MHz; $CDCl_3$–CD_3CN) 7.46 (6 H, m, 3-, 4-, 5-, 3′-, 4′-, 5′-H) and 7.90 (4 H, br d, 2-, 6-, 2′-, 6′-H). Evaporation of the ether extract gave (**1a**) (2 g).

(*Diacetoxyiodo*)*benzene*. The nitrating mixture was added to a solution of (**1d**) (2.5 mmol) in dichloromethane (0.5 cm^3) at − 20 °C (mol ratio of substrate:nitric acid:acetic anhydride: trifluoroacetic anhydride = 1:3:5:2). The three peaks centred at δ 8.2 indicated the presence of two non-bridged iodine(III) derivatives. Crystallization occurred and the crystals were filtered off and shown (n.m.r.) to be (**1a**). Reaction of (**1d**) with nitric acid was also carried out in dichloromethane on a 5 mmol scale by (i) stirring at ambient temperature and (ii) heating under reflux for 1 h. Both reactions after removal of the solvent gave an oil, δ(90 MHz; $CDCl_3$) 2.10 (s, Me), 7.67 (3 H, m, 3-, 4-, and 5-H), and 8.26 (2 H, br d, 2- and 6-H). The integral ratio of the acetate methyl peak to the aromatic peaks decreased from 0.55:1 to 0.33:1 on standing over sodium hydroxide and silica gel. Recrystallization over 15 h from dichloromethane gave (**2b**), m.p. 106 °C (lit.,[8] m.p. 105—106 °C); δ(90 MHz; CD_2Cl_2) 7.50 (3 H, m, 3-, 4-, and 5-H) and 7.88 (2 H, br d, 2- and 6-H).

A solution of (**1a**) (1 mmol), (**2b**) (0.5 mmol), and sodium methoxide (1 mmol) in dichloromethane (5 cm^3) was stirred for 1 h at ambient temperature. Sodium trifluoroacetate was filtered off and the solution evaporated and the residue recrystallized from dichloromethane to give (**2c**).

Oxidation Reactions of (**2c**).—A solution of *o*-cresol (20 mg, 0.2 mmol) in dichloromethane (0.5 cm^3) was added to a solution of (**2c**) (57 mg, 0.1 mmol) in dichloromethane (1 cm^3) at ambient temperature. The solution turned yellow-brown. The solvent was evaporated off and n.m.r. analysis showed that iodobenzene and 2-methyl-1,4-benzoquinone had been formed. Reaction with hydroquinone gave iodobenzene and benzoquinone. No reaction occurred with mesitylene even after heating the solution for 1 h at 50 °C.

X-*Ray Measurements*.—Preliminary precession and Weissenberg photographs indicated a monoclinic crystal, space group $P2_1/n$ (No. 14). Measurements were then obtained on a Picker four-circle diffractometer, using Zr-filtered Mo-K_α radiation (λ = 0.710 69 Å). The crystal was mounted on the *c*-axis in a Lindemann tube. The unit cell was refined by least-squares using 12 measurements in the range 2θ = 15—31°. The crystal data at 20 °C were: $C_{14}H_{10}F_3I_2NO_6$, M = 599.0, a = 19.585(5) Å, b = 11.561(3) Å, c = 8.243(2) Å, β = 100.38(2)°, V(cell) = 1 836.0(7) $Å^3$, Z = 4 molecules, D(meas) = 2.12 g cm^{-1}, D(calc) = 2.17 g cm^{-1}. The crystal dimensions were 0.15 × 0.275 × 0.444 mm. Intensity measurements were completed over 2 octants in the range 2θ = 0—40°. Three reflections (006, 040, and 600) were used as intensity standards and measured before each batch of 50 reflections. Two crystals were used and there was evidence of crystal decomposition, through yellowing of the initially colourless crystals, and through marked decline of the sum of the intensity standards to approximately 50% of the initial value. The second crystal gave a complete set of data which led to a lower final R value than the combined data, and was therefore adopted exclusively. The scan was in 200 steps of 0.01° in 2θ counting for 0.25 s per step with a background counting time of 25 s at each end of the scan. 1 713 Independent measurements were made. The intensities were corrected for Lorentz and polarization effects and for absorption by numerical integration using a 10 × 10 × 10 Gaussian grid. The crystal face indices and perpendicular distance from a central origin to the faces were: $\pm(2, 0, -1)$, 0.2224 mm; $\pm(110)$, 0.0750 mm; $\pm(1, -1, 0)$, 0.1375 mm. The absorption coefficient was 36.4 cm^{-1} and the transmission range was 0.383—0.624.

Structure Determination.—The programs used were SHELX-76,[14] ORTEP,[15] and some locally written programs. The phase problem was solved by direct methods. The atomic scattering factors were those incorporated in SHELX-76 together with the iodine curve from the International Tables.[16] The atoms lighter than the iodine were located by the use of electron-density difference maps. Hydrogen atoms were not found. The phenyl rings and O(1) were given isotropic temperature factors. The other atoms were given anisotropic temperature factors. After seven cycles of refinement, and at an R value of 0.11, the data from crystal 2 were found to be better than the composite data and were adopted exclusively. Refinement was continued by least-squares, minimizing $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F) + 0.004F^2]$, until convergence was reached (max. shift/e.s.d. = 0.038). 13 Anisotropic and 13 isotropic atoms, and a scale factor gave 170 parameters which were determined using 1 304 measurements, 409 measurements for which $I < 2\sigma(I)$ were finally suppressed. The residuals were R = 0.0724, R_w = 0.0945. The final difference map had a maximum of 2.00 e $Å^{-3}$, and a minimum of −1.32 e $Å^{-3}$. Fractional atomic co-ordinates are given in Table 1.*

Acknowledgements

We thank the National Sciences and Engineering Research Council of Canada for financial support.

---

* *Supplementary data* (see section 5.6.3 Instructions for Authors, in the January issue). Thermal parameters, selected intermolecular distances, and a comparison of bond lengths with literature values have been deposited at the Cambridge Crystallographic Data Centre.

References

1 R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1970, 347.

2 A. Fischer, D. L. Fyles, G. N. Henderson, and S. Ray Mahasay, *Can. J. Chem.*, 1986, **64**, 1764.

3 G. W. Bushnell, A. Fischer, G. N. Henderson, and S. Ray Mahasay, *Can. J. Chem.*, 1986, **64**, 2382.

4 P. N. Ibrahim, unpublished work.

5 J. Gallos, A. Varvoglis, and N. W. Alcock, *J. Chem. Soc., Perkin Trans. 1*, 1985, 757.

6 N. W. Alcock and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1979, 851.

7 N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 1963, 4103.

8 W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 1960, 3350; *Proc. Chem. Soc.* (*London*), 1960. 71.

9 A. Varvoglis, *Chem. Soc. Rev.*, 1981, **10**, 377.

10 E. B. Merkusev, T. I. Kogai, L. G. Polyakova, and A. N. Novikov, *Zh. Org. Khim.*, 1973, **8**, 436.

11 M. Schmeisser, E. Lehman, and D. Naumann, *Chem. Ber.*, 1977, **110**, 2665.

12 N. W. Alcock, W. D. Harrison, and C. Howes, *J. Chem. Soc., Dalton Trans.*, 1984, 1709.

13 J. Buckingham (ed.), 'Dictionary of Organic Compounds,' Chapman and Hall, London, 5th ed., vol. 3.

14 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

15 C. K. Johnson, ORTEP: a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

16 D. T. Cromer and J. T. Waber, 'International Tables for *X*-Ray Crystallography,' vol. IV, Kynock Press, Birmingham, England, 1974, pp. 99 and 148.

Received 5*th October* 1987; *Paper* 7/1771